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SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

L. C. Scala and G. D. Dixon

December 31, 1967

Contract No. 951525

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Westinghouse Electric Corporation
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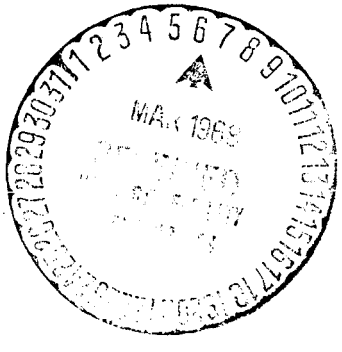
Pittsburgh, Pennsylvania 15235

Sixth Quarterly Report

Period: October 1 to December 31, 1967



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ABSTRACT

The investigation of the effect of varied zirconium oxide loadings in the coating of Webril tape for battery separators showed that: a) higher oxide loadings result in faster electrolytic diffusion; b) lower restivities are also a result of high oxide loadings; c) the coatings, however, tend to be more prone to cracking. Best results seem to be obtained at a 3:1 oxide:polysulfone ratio, at a speed of 3-4 ft/min. Ball milling the coating mixtures for several days results in smoother coatings and better filling of the Webril tape voids.

Long term exposure to concentrated KOH of battery separator material containing polysulfone 361 instead of polysulfone 1700 as binder indicated that PS 361 dissolves almost completely in the caustic. Separator material containing PS 1700, however, withstands the sterilization cycle satisfactorily.

The continuous coating apparatus is being modified to allow dip coating of the basic tape instead of doctor knife coating.

The polarograph has been calibrated to test for silver ion diffusion.

I. INTRODUCTION

This Quarterly Report covers the work done during the period October 1 to December 31, 1967. The effort expended during this time and reported here includes:

1. Investigation of the effect of variations in formulations and coating techniques.

2. Investigation of additional separator materials.

3. Sterilization tests.

4. Polarography

II. PROGRESS

1. Variations in formulations and in coating techniques

a. Effects of variation of oxide loading

Two experimental continuous runs were made in which the oxide: polysulfone ratios were 3:1 and 4:1 by weight. The mixtures were ball milled for 12 hours before coating in the continuous coating tower. Extractant bath was 1:3 water:dioxane.

The first run (C58-21-2, 3:1 oxide:PS) gave best results at a speed of 3 feet per minute; at one foot per minute there occurred excessive running of the coating mixture along the edges of the Webril tape. After several feet of tape had been coated at 3 ft/min, the extracting bath was removed to check the possibility of using heat as the sole means of eliminating the solvent (DMAC). However, the existing banks of heating lamps were not sufficient to dry the coated tape completely, so that severe blocking occurred.

During this run the gap at the knife edge metering the mixture onto the tape (originally set at 3 mils) had widened on one side, so that the coating was uneven, that is, it was much thicker on one edge. Therefore resistance and electrolyte diffusion rates values were taken both on samples of the original tape and on samples whose thicker edge had been previously cut off. Table I gives thickness and resistivities of original samples (at 3 ft/min) and Table II those of the samples with an edge cut off (3 ft/min). Samples were cut at intervals of about 2 feet along the coated tape.

Table I

Electrical Properties and Thickness of Original Samples from Run C58-21-2

Sample No.	Resistance, ohms	Specific Resistivity ohm-cm Average	Thickness mils	Ave. Thickness mils
1	5,7,7	135	4.0-8.6-4.6-4.0-7.9	5.82
2	5.4,4	102	5.2-4.7-5.3-5.8-4.6	5.12
3	4,3,3	83	6.6-4.0-4.4-6.1-4.1	5.04
4	3,2,2	71	5.5-4.7-5.6-5.8-4.7	5.26
5	2.4,4	75	4.8-6.9-4.6-4.2-6.9	5.48

Table II

Electrical Properties and Thickness of Cut Samples from Run C58-21-2

Sample No.	Resistance, ohms	Specific Resistivity ohm-cm Average	Thickness mils	Ave. Thickness mils
1	2,5,4	110	3.8-4.7-4.4-3.8-5.2	4.4
2	5,3,3	117	3.7-4.4-4.2-4.4-4.5	4.25
3	4,5,6	138	3.7-5.0-4.6-4.2-5.0	4.5
4	4,5,4	119	3.7-4.8-4.1-3.5-4.5	4.2

The resistance results shown on Tables I and II were obtained using the relatively coarse conductivity bridge mentioned previously. In all cases the specific resistivity values were below the upper limit set by the sponsor.

Measurement of the rate of electrolyte diffusion through the five samples obtained originally from Run C58-21-2 indicates a large spread of values obtained from samples coming from the same portion, run at relatively even speed and under presumably identical conditions, which may of course be attributed to the thicker edge due to unintentionally wider gap; in fact, the elimination of the thick edges reduced the spread of the electrolyte diffusion values. In both cases the rate of diffusion was rather low.

Continuous run C58-24-1 was made using an oxide:PS ratio of 4:1, the other parameters remaining the same as in C58-21-2. The mixture had been ball milled for 24 hours. Speeds of 2, 3 and 4 feet per minute were employed. At 2 ft/min the thickness in the center of the tape was 3 ± 0.2 mils; the tape edges were very thick and had not been dried by the heating lamps by the time they reached the take-up roll. At 3 ft/min the center thickness was 4 ± 0.2 mils, and the tape looked relatively good, with fully coated center and somewhat thicker edges. At 4 ft/min the edges were unevenly coated and crusty. At all the speeds the surface of the coated tape felt grainy but did not chalk or crack. The electrolyte diffusion rates of samples (2,3,4 ft/min) from the same run indicate that (1) high oxide loading results in faster electrolyte diffusion and that (2) 2 and 3 ft/min coating speeds seem to make no difference in the porosity of the experimental separators; a coating speed of 4 ft/min appears to reduce the rate of electrolyte penetration, at least under the conditions of these experiments. Table III gives some other properties.

Table III

Electrical Properties and Thicknesses of Sample from Run C58-24-1

Coating Speed ft/min	Resistance, ohms	Specific Resistivity ohm-cm Average	Thickness mils	Ave. Thickness mils
2	3,2,3.5	106	4.4-3.1-3.3-4.4-3.2	3.5
3	2,3,4	96	4.5-3.8-3.7-3.8-3.5	3.9
4	24,40,49	1140	3.8-4.5-4.0-3.6-4.0	4.0

The unexpectedly high specific resistivity value of the portion run at 4 ft/min cannot be explained easily. During the resistance measurements of the latter sample it was noticed that the sample appeared to dry almost immediately after removal from the KOH soaking bath. This phenomenon, which had never been observed before, may be explained by the fact that the 4 ft/min portion had been coated last and that at this time the relative concentration of the oxide in the mixture may have increased appreciably, possibly because of solvent evaporation, or settling out of the oxide.

b. Effect of time of soaking in KOH on resistance

The effect of KOH soaking time on resistance of experimental separator materials was studied next. The sample used was part of sample 1 (Run C58-21-2); it was soaked for 24 hours in KOH and then tested using the coarse conductivity bridge. This measurement gave a resistance value of 280 ohms. The same piece was tested with a new, more precise meter (Yellowspring Co., Model 31), which gave a resistance of 300 ohms. It was then placed in the resistivity cell in the presence of 40 percent KOH and its resistance measured as a function of time. The results show that, in the case of the relatively thick sample, prolonged exposure to 40 percent KOH brings about a decrease in resistance of more than one order of magnitude. This implies that lower resistivities than expected might be encountered in a battery after some actual operation time. In addition, these experiments indicate that it would be advisable to soak all samples at least 48 hours in order to arrive at meaningful, steady resistance values.

c. Effect of long term ball milling

A continuous run was made (C58-25-1) using a coating mixture (C58-23-2) which had been ball-milled for 8 days. This mixture consisted of the usual polysulfone 1700:DMAC solution in the presence of oven dried 20-50 mesh Bio Rad zirconia, in an oxide:polysulfone ratio of 4:1. The applicator knife's gap was 3 mils, and the extractant bath consisted of water:dioxane (1:3). Only one coating speed was used, 3 feet per minute.

The resulting coated tape was very smooth, but it retained an appreciable amount of solvent. When dry, the coating appeared to be brittle and easy to break off the Webril. Specific resistivity and ion diffusion tests were made of four samples, the first of which was taken at the beginning of the run. Table IV shows the specific resistivities and the thicknesses of 3 of the 4 samples.

Table IV

Specific Resistivity and Thickness of Tape from Run C58-25-1

Sample No.	Thickness* mils, ave.	Specific Resistivity ohm-cm	Comments
1	3.96	785	Presoaked 18 hrs in 40% KOH
2	3.90	768	Presoaked 4 days in 40% KOH
3	4.04	980	Presoaked 6 days in 40% KOH

*Average of five readings

The high values of resistivity and thickness, the relatively low rate of electrolyte diffusion and the stiff, brittle coating all indicate that 4:1 oxide:PS loading ratio is excessive. On the other hand, the prolonged ball milling did result in uncommonly smooth coatings.

A second continuous run (C58-27-2), in which the oxide:polysulfone ratio was reduced to 2:1, and which had been ball milled for 57 days, was made. The applicator knife's gap was again 3 mils originally. At a speed of 3.5 feet per minute the coating was being spread smoothly, but the voids in the Webril looked as though they were not being coated over. The thickness of the coated tapes was only 2 mils. The coat dried completely before arriving at the take up roller, it was solid and not chalky.

Because the Webril tape voids appeared not to be coated over, the applicator's gap was opened to 4 mils in order to increase the amount

of material deposited on the tape. The speed was increased to 5 feet per minute. The thickness of this coating decreased to an average of 1.9 mils, and more holes were filled. Leaving the gap at 4 mils, the speed was reduced to 3.5 feet per minute. The resulting dry coat had an average thickness of 2.2 mils and all the Webril holes appeared to have been filled. Overall, the coating film was strong, smooth, non-chalking. Table V gives the specific resistivity and thickness values of the above samples.

Table V

Specific Resistivity and Thicknesses of Samples from C58-27-2

Speed ft/min	Thickness, mils (ave.)	Specific Resistivity, ohm-cm
3.5 #1	2.28	1640
3.5 #2	2.22	1000
5	2.06	241

Interpretation of the results from this run leads to contrasting conclusions. The reduction in oxide content from the content of run C58-25-1 increased the specific resistivity of the two sample portions coated at low speed: correspondingly, the electrolyte diffusion rate was slow at both low speed runs, whether they were made with an enlarged applicator gap or not. This occurred even though it appeared that some of the largest voids in the Webril tape were not being coated over at a knife gap of 3 mils; this should have been followed by a correspondingly high diffusion rate, which did not happen. On the other hand the run at 5 feet per minute gave coated tape that possessed relatively low specific resistivity and high diffusion values. Overall, this run showed that a reduced oxide content gives thinner coatings even at higher applicator gaps; the very finely ground coating mixture actually does a better job of coating the large voids in the Webril than mixtures ground for a shorter time.

It must be mentioned that the latter batches of experimental Webril are considerably worse than the initial ones as far as homogeneity, size and distribution of voids, and constancy of thickness are concerned. The work done after this point has used new batches of 3 inch wide Webril, which has been claimed to be more uniform and generally better by the manufacturer.

d. Variations in coating techniques

A continuous run was made (C58-23-1) in which the extracting bath was not used. The coating tower was modified in such a way as to lengthen the path of the coated tape from the pay-off roller to the take-up roller. This was done in order to increase the number of heat lamps to 2 banks of 4 lamps each, on either side of the tape. The knife gap was set at 3 mils, speeds of 2, 3 and 4 ft/min were tried, and the oxide:PS ratio was 3:1.

The first problem encountered was caused by the large and dangerous concentration of DMAC fumes generated by the heating of the just-coated tapes. Fans were employed to direct the hot fumes into a hood, but this measure was largely ineffective. Any future coating that involves heating of coated tapes must be conducted under an efficient hood.

The second and more serious problem consisted of the inability of the heat lamps to dry the coated tape to such a degree that the tape would not block when wound around the take-up roller. This drawback will be overcome by installing a long furnace, either vertically or horizontally, to replace the heating lamps. This step might result in more even heat output.

Another drawback which was encountered constantly in the course of the coating experiments was the fact that the zirconia: polysulfone:DMAC mixtures often prove difficult to apply homogeneously through a Gardner Knife because of poor blade alignment, a filtering effect of the oxide out of the mixture and other generally bothersome effects. Therefore it was decided to test a dip coating method using

grooved pins to distribute the coating evenly, and a vertical furnace to dry and set up the coating rather than using a bank of heating lamp. Work is in progress to modify the existing coating apparatus along the lines mentioned above.

2. Investigation of new battery separator ingredients

a. Webril

Irregularities in diffusion rates and resistivity values have been observed frequently, and the doubt arose as to whether the thickness of the Webril tape is as constant as claimed. Therefore a piece of Webril measuring 6 x 2.5 inches was cut and thickness measurements taken on spots located on the tape as follows: four columns of 9 measurement positions, each located along the length of the tape sample; the distance between each measurement position column is slightly more than one half inch, which is also the distance between rows of positions. It was found that the thickness varied from a minimum of 1.4 mils to a maximum of 2.1 mils, with high and low values frequently very close to each other, and no particular concentration of high or low spots. A call to Kendall revealed that the Webril tape used until now belonged to an experimental and therefore uneven batch; however, the new production batch recently received by us (3 inch wide) appears to have fewer and smaller voids; its average thickness is more constant, but it is closer to 1.9 mils than to the originally claimed 1.4 mils. Since these tapes were machine cut, their edges are smooth, even and free of visible stresses.

b. Polysulfones PS 360 and 361

Polysulfones 360 and 361 (3M Company) had been acquired sometime ago because it was claimed that their structures did not possess the relatively temperature sensitive isopropylidene group. Attempts were made to dissolve those resins (361 as a free flowing, fine powder and 360 in the form of granules) in DMAC. At a solids concentration of about 13% neither dissolved easily or completely. At 9% solids concentration Polymer 361 dissolved almost completely, but the solution was not clear. Polymer 360 did not dissolve completely at 9% concentration.

Disregarding the unclear appearance of the 9% 361 solution, the latter was used to prepare coating mixtures in which the oxide:PS ratio ranged from 2:1 to 4:1. The oxide used here was again 20-50 mesh BioRad zirconia, a newly received supply.

Continuous run C58-27-1 was made using mixture C58-26-3 (45g Polymer 361, 450g DMAC, 90g dried zirconia, oxide:PS ratio = 2:1). Polymer 361 had been dried for 2 days in vacuo at about 100°C before solution in DMAC, and the whole mixture was ball milled for 90 hours. The applicator's gap was 3 mils and the extracting bath was 1:3 water: dioxane. At coating speeds of 2 and 3 feet per minute the coated tape was tacky and the voids were not completely filled. At higher speeds the tackiness increased considerably. In general the coatings appeared too thin and inhomogeneous so that no samples were taken for resistivity and ion diffusion tests.

Continuous run C58-29-1 was carried out using the same formulation as C58-27-1, except that the oxide: 361 ratio was 3:1 (mixture number C58-26-4). The knife gap was 3 mils. At 3 ft/minute the coated surface was very grainy and many of the Webril voids appeared uncoated. The thickness of this coated tape was about 3 mils. At 6 ft/min. the coating improved in that more voids appeared filled in, but the tape did not have time to dry sufficiently. In the course of this portion of the run one of the heating lamps blew up, thus pointing out the desirability of installing an upright furnace instead of the heating lamp banks used until now. At 4 ft/minute the holes were not yet completely filled; however, the coating was very smooth and even, although not homogeneous. The electrolyte diffusion time for this sample is very satisfactory. Table VI shows that resistivities and thickness values obtained from this run are satisfactory.

Continuous run C58-30-1 was made using the same formulation as C58-27-1 except that the oxide:361 ratio was 4:1 (mixture number C58-26-5). At 2 and 3 feet per minute the coating appeared to fill in the Webril voids best of all; however, the resulting coated tape was

too stiff and brittle, so that it could not be rolled properly. No samples for ion diffusion and resistivity value tests were taken.

Table VI

Specific Resistivities and Thicknesses of Samples from C58-29-1

Speed ft/min	Thickness mils (ave.)	Specific Resistivity ohm-cm
2	3.18	68
4	3.35	46
6	3.3	17.7

The fact that none of the formulations mentioned above containing Polymer 361 in 9% solids solutions really succeeded in filling the holes and voids in the new Webril tape led us to think that the amount of polysulfone in the mixture was too low. Therefore three mixtures were prepared using a 13% solution of Polymer 361 in DMAC (this corresponds to the usual 15g PS:100g DMAC). The three formulations were distinguished by having oxide:PS ratios of 2:1, 3:1 and 4:1.

Continuous run C58-31-1 (3:1 oxide:PS) used a mix ball milled for 67 hours. Knife setting was 3 mils. At 3 feet per minute a good looking film was obtained, which exhibited very few pinholes, was evenly coated and had a gritty feel. Center thickness was 3-3.5 mils. At 5 feet per minute the film did not dry very well and the coating appeared less even. The film could be bent through 180^{o} without flaking. A heavy deposit of filler remained on the knife blades, possibly due to a filtering out action. The first 3 feet of coated tape exhibited a smooth glassy surface on both sides. This material probably still contained some solvent. Its electrolyte diffusion values were acceptable. Table VII gives some other properties of the run.

Table VII

Specific Resistivity and Thickness of Tape from Run C58-31-1

Speed ft/min	Thickness mils (ave.)	Specific Resistivity, ohm-cm	
3	3.45	189	heat dried only
3	3.06	550	RT dried
3	3.06	860	RT dried
5	2.98	31	RT dried
3	3.3	38	last section

Continuous run C58-31-2 used mixture C58-30-3, in which the oxide:PS ratio was 4:1, the other ingredients remaining constant. It was soon obvious that this oxide loading was excessive; the mixture did not spread out evenly, the coated tape did not dry rapidly (thick oxide coating retained some solvent) and the excessive oxide easily precipitated out of the mixture and clogged the knife gap. As a result, the Webril tape tore frequently. No samples were taken of this run. The last run of the period was C58-31-3, which used a mixture in which the oxide:PS ratio was 2:1. The knife gap was again set at 3 mils. At 2-2.5 feet per minute the coating film was very thin and contained many pinholes. The oxide seemed not to be evenly spread. At 3 feet per minute the film looked good, glossy, and showed few pinholes. However, it did not dry properly. A coating speed of 4 feet per minute gave a thin, even film with some pinholes. Drying of the coat was not complete. At 6 feet per minute the coated tape was traveling too fast for drying. While the electrolyte diffusion rates were in general satisfactory, the specific resistivity values from all samples of run C58-31-3 are above the maximum allowed 150 ohm-cm.

3. Sterilization tests

The resistance to sterilization in hot concentrated caustic was determined for several samples of separator material obtained from

eight selected continuous coating runs. The samples from separator materials which were obtained at several speeds from each coating run, were cut to 2 x 1.5 inch size and sterilized in 40% KOH for 60 hours at 135°C. The coating runs from which the samples are derived are identified in Table VIII.

The containers, in which the samples to be sterilized were placed in contact with 40% KOH, were stainless steel cups with Teflon liners. They were sealed by steel covers, Teflon washers and C clamps, and exposed to heat in a box containing sand. The procedure and the apparatus involved are described in detail in Dr. Langer's First Monthly Report.

The effect of hot caustic sterilization on separator membranes was measured in terms of:

1. Specific resistivity before and after sterilization
2. Weight before and after sterilization
3. Thickness before and after sterilization

A sample of a new Webril fabric batch recently received, and claimed to be more uniform than the earlier type, also underwent the sterilization cycle, mainly to determine its weight loss. Since Dr. Langer found that the polysulfone PS 1700 weight loss from sterilization was negligible, it was assumed that the weight losses observed in this work were due only to the dissolution of the oxide and of the Webril into the KOH. By determining how much weight Webril would lose, the oxide weight loss could then be determined. It must be noted, however, that the resistance of polysulfone 361 to hot caustic was not determined, but it was assumed to be as negligble as that of PS 1700.

Table IX gives the results of the sterilization cycle of a total of 16 coated samples and of plain Webril.

The data shown in Table IX indicate that Polysulfone Polymer 361 is not suited for use as a binder in battery separators which must withstand

TABLE VIII

Identification of Samples for Resistance to Sterilization Tests

Sample No.	Polysulfone	Oxide: PS Ratio	Coating Speeds, ft/min.	Comments
C58-18-1	PS 1700	2:1	2, 3, 6	Ball milled 9 days
C58-21-2	PS 1700	3:1	3	Ball milled 10 hours
C58-24-1	PS 1700	4:1	2, 3	Ball milled 24 hours
C58-25-1	PS 1700	4:1	3	Ball milled 8 days
C58-27-2	PS 1700	2:1	5	Ball milled 57 days
C58-29-1	P 361	3:1	2, 4, 6	Ball milled 7 days New Webril
C58-31-1	P 361	3:1	3, 5	Ball milled 67 hours, New Webril
C58-31-3	P 361	2:1	2, 3, 6	Ball milled 27 hours, New Webril

TABLE IX

Results of Sterilization Tests on Selected Separator Materials
Sterilization cycle: 60 hours at 135°C in 40% KOH.

Sample No.	Coating speed, ft/min.	Thickness before sterilization, mils	Thickness after sterilization, mils	Weight change after Sterilization, %	Specific resistivity before sterilization, ohm-cm	Specific resistivity after sterilization, ohm-cm	Comments
C58-18-1	2	3.2 3.4 3.25 3.5 4.9	3.3 3.4 3.5 3.65 4.6	-8.5	75	59	No change in physical characteristics of separator and of KOH solution.
C58-18-1	3	3.7 3.55 3.5 4.45 4.42	3.4 3.65 3.6 3.5 5.2	-7.4	73	59	"
C58-18-1	6	5.5 3.95 3.8 3.40 3.45	4.6 3.7 3.7 3.55 3.0	-8.7	73	34	"
C58-21-2	3	3.9 4.0 3.85 3.65 4.05	4.3 4.2 3.75 3.3 3.95	-7.4	83	--	"
C58-24-1	2	4.0 4.0 3.85 3.6 4.4	3.9 3.2 3.4 3.65 2.9	-9.0	106	--	"
C58-24-1	3	4.7 4.8 3.75 3.45 3.3	3.7 4.0 3.1 3.3 2.8	-8.7	96	--	"
C58-25-1	3	4.55 3.8 4.2 4.05 3.8	4.35 3.85 4.3 4.1 3.7	-9.6	785	--	A crease in separator appeared, likely caused by pressure from cell cover. Some flaking at crease.
C58-27-2	5	2.0 2.0 2.1 2.0 1.95	1.95 1.9 1.95 1.8 2.0	-16.2	240	400	No change in separator. KOH solution slightly yellow

TABLE IX (cont)

Results of Sterilization Tests on Selected Separator Materials
Sterilization cycle: 60 hours at 135°C in 40% KOH.

Sample No.	Coating speed, ft/min.	Thickness before sterilization, mils			Thickness after sterilization, mils			Weight change after Sterilization, %	Specific resistivity before sterilization, ohm - cm	Specific resistivity after sterilization, ohm-cm	Comments
C58-29-1	2	2.2	2.5	2.2	1.75	2.0	1.8	-33	68	85	Both KOH solution and sampl are yellow. Sample resembles plain Webril. Coating is no
		2.15		2.1	2.0		2.0				
C58-29-1	4	2.2	2.6	2.35	1.75	2.1	2.3	-43	46	108	"
		3.45		3.3	1.8		2.25				
C58-29-1	6	3.2	3.2	3.0	1.9	1.95	1.9	-51	18	130	"
		3.2		3.25	1.8		1.85				
C58-31-1	3	3.8	4.15	3.6	2.0	1.9	1.9	-65	31	--	"
		3.15		3.9	1.8		1.6				
C58-31-1	5	3.0	3.05	3.4	2.0	2.0	1.9	-54	38	66	"
		2.8		2.7	2.05		1.6				
C58-31-3	2	3.5	3.3	3.3	2.35	2.1	2.0	-58	37 (700)	130	"
		3.4		3.1	1.9		2.1				
C58-31-3	3	2.35	2.5	2.35	2.0	2.0	2.2	-38	290	120	"
		2.4		2.55	1.8		1.75				
C58-31-3	6	2.75	3.0	2.7	1.9	2.15	1.95	-58	260	130	"
		3.4		3.05	2.4		1.80				
Plain Webril	-	1.7	1.8	1.9	2.0	1.8	1.9	-1.7	--	--	KOH solution is slightly yellow. Sample unchanged except for curling at edges.
		1.7		1.65	1.8		2.0				

attack by hot, concentrated caustic. Indeed, samples from C58-29-1 down, all containing PS 361, lost all their coating as indicated by their elevated weight losses and reduction in thickness after sterilization. KOH damage was also demonstrated by the presence of yellow color both on the separator sample and in the KOH solution, after sterilization. However, this color could be washed off the samples, which then resembled very closely the original, plain Webril tape. The thickness values after sterilization indicated very strongly that all that remained was Webril, and that the coating mixture went completely into solution.

The situation is quite different in the case of the coating mixtures containing polysulfone P 1700. Here the thickness of the coated samples before and after sterilization remained generally constant and no change was detected in the separators after sterilization. In some cases the sample resistivity readings were so close to the blank readings that no values were recorded. The weight losses were fairly constant at around 8-9 percent, from which the weight loss exhibited by plain Webril should be subtracted. If operation of the sterilizable battery can withstand it, saturation of the KOH solution with free zirconia would probably reduce the weight loss of separators. In any case, this level of weight loss might not be significant in terms of resistivity and mechanical characteristics; it might, however, be important with respect to silver and zinc ions diffusion. This will be tested later.

4. Determination of silver ion diffusion through a membrane

A continuous method of silver ion determination was required which would not involve a change in the volume of the solutions under study. The method of analysis chosen was that of polarography. The instrument used was a Heath built polarograph, model EUW-402 M employing a dropping mercury electrode (DME) as the working electrode and a massive, external mercury-mercuric oxide electrode (in 40% KOH) as the reference and counter electrodes. This allows one to scan from 0 v to -1.5 v with

respect to the counter electrode. The cathodic step due to silver ions coincides with the limiting value of the polarogram, arising from the anodization of mercury.

The limiting or diffusion current for 40% KOH is 0.025 μA. With silver ions dissolved in 40% KOH, the diffusion current increases linearly with increase in silver ion concentration. A saturated silver solution was prepared by dissolving silver nitrate in 40% KOH. After filtering, portions of this solution were diluted to different extents with 40% KOH. Each solution was analyzed by a 'wet' chemical method and a polarogram also obtained. The chemical analysis was carried out as follows: The sample was acidified to 0.1N with respect to nitric acid. The silver was extracted with dithizonate in carbon tetrachloride. The excess dithizonate was removed from the carbon tetrachloride with dilute ammonium hydroxide and the determination was completed by spectrophotometric measurement of the residual silver dithizonate colors.

The following results have been obtained:

Table X

Calibration of Polarograph for Detection of Silver in 40% Caustic

Sample	Silver content by the dithizonate method, p.p.m.	Silver content less blank, p.p.m.	Diffusion current, 10^2 μA	Diffusion current corrected for blank, 10^2 μA
40% KOH blank	0.9	-	2.5	-
Silver sol. 1	3.8	2.9	15.1	12.6
Silver sol. 2	9.6	8.7	20.6	18.1
Silver sol. 3	23.4	22.5	35.8	33.3
Silver sol. 4	51.3	50.4	63.5	61.0

At present, work is in progress in designing apparatus for continuous monitoring of solutions as silver ions diffuse through a membrane.

Future Work

1. Continue modification of coating apparatus.
2. Test feasibility of dipping method for coating Webril tape.
3. Continue investigation of ion diffusion rates through separator membranes.